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CAMOUFLAGE BY CONTROLLABLE COLOR
CHANGES

J. E. Gilligan, et al

IIT Research Institute

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approaches, the state-of-the-art in materials technology, and of the requirements of the program, a liquid crystal approach was deemed to have the best potential for demonstrating the feasibility of a variable camouflage system. Other approaches, though they may eventually prove feasible, could not have been demonstrable within the time frame of the program.

By electrically varying the temperature of a cholesteric liquid crystal, the color is also varied. The concept has been demonstrated to be reversible, controllable and reproducible, even though the colors and color ranges obtained are not ideal.

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TECHNICAL REPORT No. LWL-CR-20C73

CAMOUFLAGE BY CONTROLLABLE COLOR CHANGES

Final Report

Contract No. DAAD05-73-C-0536

By

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April 1974

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U.S. Army Land Warfare Laboratory
Aberdeen Proving Ground, Maryland 21005

iii.

SUMMARY

The objectives of this program were to explore various concepts for a controllable, variable color camouflage system, to select whichever concept exhibited the greatest near-term potential, and to construct a device/model to demonstrate the feasibility of that concept. Of all the concepts examined, that of using liquid crystals appeared to have the most promise for an early practical demonstration. Certain cholesteric liquid crystals, and mixtures of them, exhibit a color which depends upon temperature. By varying the temperature of the liquid crystal (or mixture) the color could thus be varied. Liquid crystals, (in this case, only cholesteric liquid crystals), exhibit color change properties which occur over a definite temperature range.

Different liquid crystals possess different ranges in which color is manifest, and most do not exhibit all the colors of the visible spectrum. A substantial effort, therefore, was devoted to obtaining pertinent information from consultants, from the literature, and from our own laboratory experiments. This work led to the determination of several useful liquid crystal systems; but more importantly the many problems involved in translating a laboratory mixture into a practical camouflage system were elucidated.

For demonstration purposes a commercially available liquid crystal film was applied to an electrically heated canvas cloth. The latter was shaped to conform to a 1/32 scale model tank. When heated to approximately 110°F, the liquid crystals become dark red in color. As the temperature is raised, the color turns to brown, then to dark green, and ultimately to a dark blue. Separate electrical circuits in the canvas permit control of the temperature, and thus of the color, of each individual zone to which the circuits supply energy.

Recommendations are made for continued work in liquid crystal technology, applications problems, infrared properties, biological systems, electroluminescence, phototropic and similar materials, and some sophisticated mechanical-electrical systems.

DEFINITIONS

- Liquid Crystal - an organic compound whose molecular structure is such that in a temperature range above its melting point the material exhibits considerable order in its molecular arrangement.
- Mesophase - the phase(s) of a liquid crystal material in which it exhibits liquid crystal properties, extending from the melting point (where it is a solid) to the temperature at and above which the molecular arrangement is completely isotropic (randomly disordered).
- Lyotropic - displaying liquid crystal properties which are developed by a solvent and dependent upon its nature and amount.
- Enantiotropic - having a stable structure within a definite temperature range; more than one structure is possible.
- Nematic - having molecular order in one plane, or alignment along one definable axis.
- Smectic - having molecular order in two planes, or alignment along two definable axes.
- Cholesteric - indicative of an ester of cholesterol; also possessing a twisted (or spiral) nematic structure.
- Colorplay - the range and color response of the variable producing it, e.g., a 5 C° colorplay implies a color shift from red to blue over a temperature range of 5C°.

TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| FOREWORD | ii |
| ABSTRACT | iii |
| SUMMARY | iv |
| DEFINITIONS | v |
| LIST OF TABLES | vi |
| LIST OF FIGURES | viii |
| 1.0 INTRODUCTORY REMARKS | 1 |
| 1. POTENTIAL CONCEPTS OF VARIABLE CAMOUFLAGE | 2 |
| 1.1 Basic Materials Requirements | 2 |
| 1.2 General Remarks | 2 |
| 1.3 Evaluation of Materials Approaches | 4 |
| 2. TECHNICAL DISCUSSIONS | 8 |
| 2.1 Analysis of Camouflage Requirements | 8 |
| 2.1.1 The Concept of Visibility | 8 |
| 2.1.2 The Practical Requirements of Camouflage | 8 |
| 2.1.3 Origin of Color - Objectively Measured | 9 |
| 2.2 Literature Search | 11 |
| 2.2.1 Scope | 11 |
| 2.2.2 General Results | 11 |
| 2.2.3 Nomenclature | 13 |
| 2.3 Literature Search Results/Reviews | 15 |
| 2.3.1 Introductory Remarks | 15 |
| 2.3.2 Discussions | 15 |
| 2.4 Conclusions | 21 |
| 2.5 Liquid Crystal Chemistry | 22 |
| 2.6 Symposium on Liquid Crystals | 31 |
| 2.7 Consultation with Dr. G.H. Brown | 33 |

Table of Contents (Cont'd)

| | <u>Page</u> |
|---|-------------|
| 3. EXPERIMENTAL ACTIVITIES | 35 |
| 3.1 Liquid Crystal Mixtures - Syntheses and Properties | 35 |
| 3.1.1 Introduction | 35 |
| 3.1.2 Experimental | 36 |
| 3.1.3 Results and Discussions | 37 |
| 3.1.3.1 Lowering of the Tri-Mixture Temperature to a Workable Temperature Near 50°C | 37 |
| 3.1.3.2 Stabilizing the Color Play | 40 |
| 3.1.3.2.1 Cholesteryl Chloride | 40 |
| 3.1.3.2.2 Cholesteryl Acetate | 41 |
| 3.1.3.2.3 Additives | 43 |
| 3.1.4 Conclusions | 45 |
| 4. DEMONSTRATION MODEL | 46 |
| 4.1 Temperature Controlled Color Panel | 46 |
| 4.2 Fabrication of a Heating Shroud for a Model Tank | 46 |
| 4.3 Demonstration Model | 48 |
| 5. CONCLUSION AND RECOMMENDATIONS | 51 |
| 5.1 Conclusions | 51 |
| 5.2 Recommendations | 54 |
| REFERENCES | 56 |

LIST OF TABLES

| <u>Table No.</u> | | <u>Page</u> |
|----------------------|---|-------------|
| 1 | LITERATURE SEARCH KEYWORDS | 12 |
| 2 | NOMENCLATURE | 14 |
| 3 | EFFECTS NOTED IN REFERENCES | 23 |
| 4 | COLORPLAY IN CHOLESTERYL CHLORIDE CONTAINING TRI-MIXTURES | 38 |
| 5 | COLORPLAY IN CHOLESTERYL ACETATE CONTAINING TRI-MIXTURES | 42 |
| 6 | EFFECTS OF ADDITIVES ON THE COLORPLAY OF LIQUID CRYSTAL MIXTURES | 44 |

LIST OF FIGURES

| <u>Figure No.</u> | | <u>Page</u> |
|-----------------------|---|-------------|
| 1 | CLASSES OF LIQUID CRYSTALS | 30 |
| 2 | SCHEMATIC OF TANK SHROUD HEATING CIRCUITRY | 47 |
| 3 | MODEL TANK IN SIMULATED DYNAMIC CAMOUFLAGE- PROGRESSIVE STAGES OF COLOR ADAPTABILITY | 49 |

1.0 INTRODUCTORY REMARKS

In discussions of the technical and administrative requirements of the program with the LWL technical monitor, Mr. Joe A. Swisher, two major objectives were elucidated: to establish one or more materials or systems of materials in which color can be varied reversibly, reproducibly and on command, and to reduce to a transportable demonstration model whatever one of these appears to have the most immediate practical potential.

Any material with an optical response to temperature, electrical fields, mechanical pressure, radiation, stress, etc., was given consideration. As the program continued, however, the effort was increasingly directed to the selection of practical materials systems, and ultimately of one which could be embodied in a transportable model.

Since the application for this effort is in the camouflaging of vehicular systems, many of the constraints and requirements associated with military vehicles were considered. Although other sources of energy may be utilized, those common to self-propelled vehicles received first consideration, viz., motive (mechanical), electrical (storage battery, generator), and thermal (exhaust heat).

1. POTENTIAL CONCEPTS OF VARIABLE CAMOUFLAGE

1.1 Basic Materials Requirements

Essentially, the major requirements of the camouflage system are these: it must be variable, reproducible and exhibit relatively fast color change in response to a controllable stimulus which is available on or can be supplied with reasonable ease by a military vehicle. The requirement that the system be continuously variable implies that the color or color change magnitude be proportional to the magnitude of the stimulus. Reproducibility means that the color will be the same at any given stimulus magnitude, irrespective of cycles. In general, however, this latter requirement can not be strictly met, since many materials exhibit hysteresis, while others "age" or wear. The system must be controllable so that color changes can be effected on command. Changes also must occur within a reasonable period of time, say, of the order of one minute (or less).

1.2 General Remarks

Many "effects" are known which involve a color change, at the materials level, upon the application of some stimulus. The optical properties of liquid crystals are affected by temperature, mechanical strain, magnetic and electric fields and by sound waves. Many substances change color as a result of a molecular rearrangement. The phototropic materials respond to light intensity: their transmittances decrease with increasing intensity; this is the principle employed in certain sunglasses. Mechanical pressure can also produce optical changes. One of the most intriguing possibilities lies in the consideration of the chameleon effect. Many animals and fish have the capability of adapting their skin colors to the colors and color patterns of their immediate environment. Nearly every inorganic material will emit visible radiation under bombardment by ultraviolet and/or more energetic radiation. Electroluminescence, the emission of visible radiation, under the influence of an applied electric field, is an additional possibility, along with electro-reflectance,

the Stark effect, and others in which applied electric fields induce emission or affect the intensity or spectrum of natural luminescence. An example of a material which exhibits field-induced emission is Gallium Arsenide. This material is used as the light emitting diode material in hand-held calculators; the emitted light is induced by a small dc voltage. These and other possible mechanisms have been considered for application in this program. The more important ones are discussed subsequently.

Variable camouflage may also be achieved on a systems level by mechanical manipulation, as with louvers, shutters, shades and movable scenarios. Obviously, the mechanical approach could be combined with a materials approach in order to offset their individual disadvantages. The mechanical approach, however, was one of the first to be eliminated from detailed consideration because such systems are not truly continuously variable. A shutter system, for example, can have a different color pattern on each element, permitting a large combination of patterns, but the color patterns of individual elements are not variable at all. The materials approach can be developed independently and its ultimate use on mechanical systems would not be prevented.

From our reviews of the literature and our general knowledge of induced optical effects in materials we can conclude in general that most of the various materials approaches mentioned previously are not viable candidates for further consideration for one or more of several reasons. Some approaches would have required extensive research and development; others, extraordinary types or magnitudes of stimuli; and still others, either a major extension of basic physics, a minor breakthrough in materials science, or an unmanageable number of high-risk experiments.

1.3 Evaluation of Materials Approaches

The optical properties of many materials can be varied by the application of pressure (Refs. 1-3). The property which varies is the magnitude of the optical absorption edge. Unfortunately, very large pressures, of the order of tons per square inch, are required to produce a noticeable shift in the absorption edge. We could question also the net effect of such a shift on visible absorption.

There exists an abundance of materials whose optical properties vary with incident radiant energy intensity (phototropic) or with temperature (thermotropic) or with both (thermophototropic). The mechanism involved in each instance is counter-productive with respect to program requirements because the optical response is not actually a color change. Rather, it is a change in the broad band visible absorption and is manifest by a gradual darkening (loss of visible transmittance). In the phototropic case the response depends upon incident light intensity, and, for this reason, does not satisfy our requirement for controllability. Thermotropic materials would be better candidates but they still suffer from the original objection, viz., that the optical response is either a lightening or darkening of the material (depending upon how affected by temperature changes). The same argument applies also to thermophototropic materials but is compounded by the possibility of either divergent or cancelling effects.

Numerous inorganic materials change color upon heating, but inevitably the change is irreversible, or very slowly reversible, and is accomplished only at high temperatures - some as high as 700°F. Tempil-stick temperature indicators are good examples of commercial uses of such materials.

Other possibilities such as electrically induced optical properties or luminescence, and magnetically induced optical changes and biological systems offer considerably more potential in the order stated. The effect of an electric field may be either direct, indirect, or both. The direct effect is exemplified by light emitting diodes (LEDs); the indirect effect, by electro-reflectance. The former, of course, has current commercial applications. To develop electrically sensitive systems meeting the program's basic requirements a substantial increase in applied research and in allotted development time would be required. Our elimination of this concept is based on the facts that the spectral characteristics of the induced luminescence of LEDs are insensitive to the inducing field magnitudes, that applied research has "aimed" at specific applications whose requirements are not consistent with those of this program, and that varying the magnitude of an electric field (or current) will very likely not shift the luminescence wavelength. From a fundamental viewpoint the difficulty lies with the fact that the position of any two energy levels in a solid material would be invariant with respect to applied fields, even though the population of electrons in any such level could be strongly affected. Exceptions may be possible in heavily doped compounds. Thus, we conclude in the case of electroluminescence and other electrically driven devices that there is potential, but the time to achievement is on a much larger time scale than that afforded by the program.

Magnetically driven devices appear to have some limited potential but the time scale to practical development is very long. The possibility can be appreciated somewhat by observing that magnetic effects on the electronic structure are very well known, e.g., in nuclear magnetic resonance spectroscopy and in electron paramagnetic resonance spectroscopy, where relatively strong fields produce effects which are observable at radio frequency energies, not at the relative energies associated with visible radiation.

Perhaps the most successful and most widely used form of camouflage is that employed by many species of the animal world - the well known and so-called "chameleon" effect. Nevertheless, not enough is known about the mechanisms of this effect to extend them to our applications, although the effect is clearly a very real and effective one. The basic question involves a lack of knowledge of the primary (and secondary) stimuli, the actual chemical, physical and/or biological changes taking place, the nature of the reflectance change, and the information relationships between them. We also want to know the nature and level of biological activity that senses a necessity for a color change, directs that color change, and senses that the change, when accomplished, satisfies the need to "look like" or blend into the immediate environment. The feasibility of the chameleonic effect as a camouflage system depends upon the nature of the directing activity in animals with this capability. If the brain directs the entire process, the effect may be useful and eventually developable as a practical camouflage system for our purposes. If, however, the directing activity is local, i.e., if each local area of the skin reacts independently of other areas, then the mechanism must be initiated locally. If this is true, then substantially more research would be necessary than if otherwise, in order to study the mechanisms involved. Such research would be very extensive, since a local effect implies that a local area has enough "intelligence" to recognize and characterize the radiation spectrum incident on it and to direct a color match to the color characteristics of its immediate environs by adjusting its skin reflectance characteristics accordingly. So effective is animal camouflage that its potential benefit in military applications must not be overlooked. Both basic and applied research on the questions we have noted here should be carried out - at least to the point of establishing the difficulty of utilizing this concept in practical military applications.

The remaining concept - liquid crystals - holds the most promise for early demonstration. Accordingly, the possible materials approaches were narrowed down to that of liquid crystals. Some are commercially available and demonstrably possess the general capability of undergoing a continuous reversible color change.

2. TECHNICAL DISCUSSIONS

2.1 Analysis of Camouflage Requirements

2.1.1 The Concept of Visibility

Effective camouflage means that an object's visibility approaches zero, or in other words that any observer regardless of position be unable to distinguish and recognize an object in a background environment, even though the background may appear differently to differently located observers. Objectively, visibility depends upon color contrasts (differential intensities of reflected colors); an object is visible if its color is detectably different from that of its immediate environment. Detectability involves both spatial resolution and visual acuity on a spectral basis. Recognition or identification implies visual perception of not only contrasts and differential contrasts but of patterns of contrast. A forest, for instance, displays a variety of colors; its trees and their foliage have different sizes and shapes and color variety. Recognition, therefore, implies geometrical as well as spectral distinction between objects of varying color, size, and shape, yet in patterns of a regular or predictable array. Effective camouflage consequently matches both color and pattern to a background.

2.1.2 The Practical Requirements of Camouflage

The practical requirements of an effective camouflage system are numerous and complex. In this program the color must also be adjustable, and changes in it must be reversible; commanded color changes must be capable of occurring in a reasonable period of time (of the order of a minute). The camouflage color must be stable, reproducible, and capable of matching the color and pattern characteristics of its environment. Matches made by varying the reflectance of the camouflage system are preferred over those made by luminescence or similar schemes.

The reflectance characteristics of a surface - specularly (different reflectance values as a result of different angles of illumination and/or viewing) and intrinsic optical properties (indices of refraction and absorption) - vary with wavelength.

Many dielectric materials possess a nearly Lambertian reflectance; that is, the angular reflected intensity follows a cosine distribution. For this reason, many of these materials appear dull or matte. Bright colors occur as a result of narrow spectral regions of high reflectance and glossy ones as a result of high first surface reflectance.

Matching a camouflage system to a specific environment, for very practical reasons, must also match the specular characteristics of that environment. The usual situation in which the natural background is diffuse consequently dictates that the camouflage systems must have a matte appearance. In no case should a camouflage system exhibit a different color, however slight, as a function of the angle of viewing it. Some general means by which diffuseness can be achieved (or how specularity can be avoided) are given in a later section.

2.1.3 Origin of Color - Objectively Measured

The basic "color" of a material is determined by its intrinsic absorption characteristics. Subjectively, of course, it also depends upon the illumination spectrum, incidence and viewing angles, and upon the visual acuity and impartiality of the observer. Light incident on a surface is either transmitted, reflected, or absorbed. The absorption coefficient and the index of refraction are the main parameters defining the macroscopic optical properties of matter.

The variation of intrinsic properties with wavelength causes some photon energies not to be as strongly absorbed as others and thereby to be colored in the non- or less- absorbing wavelength regions. The spectrum of radiation which is not absorbed obviously determines the color. A material which absorbs no incident visible radiation is either "clear" (transmitting) or "white" (reflecting). The origin of color, therefore, is in selective spectral absorption.

There are two additional factors of central importance to this study. One is the nature of the absorption band which causes spectrally adjacent regions to be pronounced and hence to define the dominant color; the magnitude and spectral location of each such band is all-important. A second is the textural and/or particulate nature of the gross material. In non-metallic materials high reflectance arises from multiple scattering processes. The scattering effect is greatest when the dimensions of scattering centers - e.g. particulates, fibers, colloids, crystallites, microcrystals, and/or the spaces between them - are roughly those of the wavelength of the incident radiation. The wavelength of maximum scattering effect is critical because the scattering can intensify the absorption effect and thus magnify the color in adjacent spectral regions. The entire basis of this study rests on the possibility of altering intrinsic properties and/or the geometrical factors which influence the scattering effect.

The manipulation of fundamental optical properties implies that the spectral index of refraction, $n(\lambda)$, and/or the spectral index of absorption, $k(\lambda)$, can be externally controlled. Altering the scattering effect through induced changes in molecular or geometric orientation, or in the macroscopic properties, of a material can produce large changes in their optical scattering properties.

Many effects are known in these two general areas, but for the application at hand, we must consider the practicality of the various stimuli which can be employed to effect color changes. In the ensuing discussions we are consciously aware of practical considerations, although they may not be mentioned specifically.

2.2 Literature Search

2.2.1 Scope

A key-word system was devised for use in a computerized information retrieval program. The initial index is shown in Table 1. The search sought to list any published document dealing with the effect of any external stimuli, specifically effects induced thermally, electrically, mechanically, accoustically, or otherwise, upon the reflectance, absorptance, transmittance or upon the intrinsic optical properties of materials. The search covered Chemical Abstracts and the Engineering Index from 1969 to the present. Because of the nature of the information sought, the Information Science specialists believed that a search of Physics Abstracts would merely duplicate other sources. A special search of camouflage literature, however, was productive.

2.2.2 General Results

The computerized literature search listed a total of nearly 1000 citations, of which about 200 were of strong interest and 50 were considered highly relevant. The initial citations had some obvious "holes" in the data. Subsequent runs were made based on more specific terminology, especially in the field of liquid crystals.

Because the initial literature search indicated that liquid crystals show the most promise as a mechanism for controlled color change, another literature search was initiated concentrating on liquid crystals and the types of stimuli which induce color change.

A review and analysis of all the literature leads us to the following observations: First, controllable and reversible color changes covering the full visible spectrum can be accomplished. Second, the alteration of intrinsic optical properties of inorganic dielectric materials via external stimuli seems at best to be a remote possibility under the requirements of this program - at least to the extent that significant (useful) color changes may be induced in any practical way. Third, the type of materials to meet this program's ultimate objectives are liquid crystals, because their properties in general are more easily varied reversibly and controllably by external stimuli than any other class of materials.

Table 1
LITERATURE SEARCH KEYWORDS

Response

Optical Response
Color Change
Reflectance
Transmittance
Absorptance

Stimulus

Electrical Field
Temperature Change
Pressure/Stress
Light (UV Radiation)

Suffixes:

Tropism
Chromism

Prefixes:

Electro
Thermo
Piezo
Radio/Photo

The majority of the relevant information obtained is published in approximately six (6) scientific journals, and, since none of it applies directly to the camouflage application here, judgments of potential applicability are more difficult to make. The discussions which ensue are based upon critical reviews of these articles and frequently on the original articles to which they refer.

The intent of this effort was to produce as large a data base as possible regarding materials in which color changes may be induced by external stimuli. A vast number of materials were found which respond by a change in their optical properties to an outside stimulus. Unfortunately, in the majority of these the color change is not reversible, continuous, or reproducible. While this particular observation came as no surprise, a number of color effects which we initially believed would not be useful may hold some promise, at least in a backup sense.

2.2.3 Nomenclature

A color change in a material can be produced by many different types of external influences. Table 2 lists some of the more common prefixes and suffixes of interest here. The meaning of each of the prefix and suffix terms is highly important to the meaning of their combinations. Distinctions, for instance, are made between thermo and pyro, and between chromism and tropism. "Thermo" implies temperature (irrespective of energy required to maintain it) and "pyro" implies thermal energy input (essentially irrespective of temperature). Tropism refers to a change in molecular structure or orientation; chromism, to a change in color. Neither of these terms implies the other, but in many instances, and certainly in the case of cholesteric liquid crystals, the chromism results from a tropism (-but not vice versa). The point is that the description via the above terminology of certain induced changes in the optical properties of a material does not necessarily imply the physical mechanism responsible for the change, and thus one must be aware that the terminology tends at best to be only loosely

Table 2
NOMENCLATURE

| <u>Suffix</u> | <u>Effect</u> |
|---------------|-------------------------------------|
| Chromism | Color change/shift |
| Tropism | Structure or conformation change |
| <u>Prefix</u> | <u>Meaning</u> |
| Thermo- | induced by temperature |
| pyro- | induced by heat |
| piezo- | induced by pressure, strain, stress |
| photo | induced by visible light |
| acousti- | induced by sonic vibrations (sound) |
| magneto- | induced by magnetic field |
| electro- | induced by electric field |

descriptive of the actual mechanisms involved. Consequently, one should interpret the literature citations and the reviews of them here in a fairly broad way.

2.3 Literature Search Results/Reviews

2.3.1 Introductory Remarks

As mentioned earlier, nearly 1000 citations were elicited from the published literature. Of these approximately 200 were found to be relevant, that is, to contain information about materials which change color under an external stimulus. We will not review here each of the articles retrieved since some were found upon close study to be unuseful, or defective; most were repetitious. In the subsequent sections we will represent a condensation of the various articles, books, and other technical publications which we have reviewed.

2.3.2 Discussions

The majority of the citations dealt either with photochromic materials (such as the spiopyrans) or with liquid crystals. Every issue of the Journal of Molecular Crystals and Liquid Crystals in the years 1971 to 1973 was scanned for relevant articles and pertinent references to earlier articles.

Adams et al. (ref. 4) state that the helical pitch in cholesteric materials is a fundamental parameter, often very sensitive to temperature, shear, electric fields and organic vapors. They trace the development of liquid crystals from 1888. The angular transmittance and reflectance properties of cholesteryl chloride-cholesteryl nonanoate mixtures were studied over a wide range of compositions and of illumination/detection angles. Amongst other conclusions they attribute the selective reflection of these liquid crystals to the helical arrangement of stacked layers.

In a mathematical treatment based on field theory, Alben (ref. 5) relates the pitch to temperature through the elastic pitch constant. He explains the temperature dependence as a "pretransition effect," an unwinding of the cholesteric helix (increasing pitch) with decreasing temperature prior to a transition from the cholesteric to a smectic phase. He further states that the temperature dependence of the reflective wavelength is typically less than 1/30th the rate of the "pretransition effect." It should be noted, however, that the sensitivity of the color-temperature relationship varies substantially from one material or mixture to another.

The relationship between pitch and temperature determines the color of a crystal at any given temperature. These authors are two of many others who have explored these relationships and who have explained the selective color effect as a diffraction phenomenon; the pitch corresponds to the diffraction wavelength. Mixtures of liquid crystals have an effective pitch which is determined by intermolecular forces.

Hirata et. al. (ref. 6) describe the results of an effort to synthesize and characterize a homologous series of hydroxy anils, starting with the nematic liquid crystal, MBBA, N-(p-methoxybenzylidene)-p-n-butylaniline. MBBA is perhaps the most popular of all the liquid crystals and has been the starting point for many investigations. The authors studied the electro-optic effects in a 50-50 mixture of o-OH substituted MBBA and N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA), noting that this mixture was more stable and had a lower electro-optic threshold than MBBA.

Berreman and Scheffer (ref. 7) report the results of reflectivity measurements made on a single-domain, binary cholesteric liquid crystal. The mixture consisted of a nematic fluid 4,4'-bis(hexyloxy)azoxybenzene and a non-mesomorphic (i.e, a non liquid crystal), but optically active, compound 4,4'-bis (2-methylbutoxy) azoxybenzene (2-MBAB) the resultant mixture is a cholesteric liquid crystal, whose pitch can be varied from infinity to 240 nm by increasing the mole fraction of 2-MBAB. The pitch is very weakly temperature dependent, and the mesomorphic range extends from 42°C to 130°C, dependent upon 2-MBAB mole fraction. This range is too large to be of use to this program.

Davison (ref. 8) has provided a rather detailed procedure for estimating heat transfer characteristics of nematic liquid crystals. The work is not especially important in this program but does give an indication of the breadth of work being accomplished in liquid crystal technology.

Williams (ref. 9) is one of many to note the formation of domains in nematic liquid crystal's upon the application of a dc voltage. He reports that, as voltage is increased, at a field strength of 1000 v/cm domains begin to appear. Williams offers a model of domain formation in nematic liquid crystals which accords reasonably well with experimental findings. His experiments were carried out using p-azoxyanisole, although he did mention somewhat comparable results with another quite commonly used liquid crystal, poly- γ -benzyl-L-glutamate. Nine years later, Williams published a paper (ref. 10) reporting electric field effects in MBBA, and again notes response times of the order of 1 sec. or less. The effects in either case are of the go-/no-go type and hence not useful to us.

A model for the reflectance spectrum of a liquid crystal has been developed by Subramanyam (ref. 11). Comparisons of calculated vs. experimental results for a solution of 70% cholesteryl nonanoate and 30% cholesteryl chloride are also presented.

If one were to design a liquid crystal with specific properties, the work of Gibson and Pochan (ref. 12) would be highly relevant, in that it typifies the effects of molecular structure on a material's properties. The work described correlates in a classic way the influence of ligand groups, their identity and location, on molecular properties. The authors point out clearly that the position, number and length of branches in the alkanoate portion of cholesteryl alkanoates profoundly affects their mesomorphic behavior. Although their paper does not give optical data, the implications of branching in this respect are reasonably deducible.

The article by Chandrasekhar and Prasad (ref. 13) develops the theory of rotatory dispersion and of circular dichroism in cholesteric liquid crystals. Though not applicable to the origin of the principal color properties, it is an informative article and the effects discussed would be of some value in the case of circularly polarized light.

Nicoll's experiments with cathodoluminescence (ref. 14) in CdS demonstrate the relatively high efficiency of injection luminescence. The spectrum (color) of the emitted light depends upon applied voltage. The emitted light is more intense than the light reflected from an object even on a very bright day. Presumably, very low temperatures are required to make this mechanism operate.

Chang (ref. 15) offers a slightly different explanation for the electric field induced domains in MBBA than does Williams (ref. 7), especially since he takes account of MBBA's negative anisotropy. Chang describes five different types of microstructure, (observable under a standard microscope).

Baily and Jennings (ref. 16) have pointed out that the molecular orientation of liquid crystals can be affected by a number of external influences. Although they are not the first to notice the effects of external stimuli, they were among the first to make electric dichroism measurements, to study the effects of pulsed AC fields both parallel and transverse to the field of liquid crystals alignment and to describe a simple technique for doing so. The dichroic effect that many liquid crystals possess, however, is one which has little, if any, bearing on their response to electric fields.

Photochromic materials have been studied extensively for many different purposes. Kiss and Phillips (ref. 17) have reported on a study in which a reflectance change, induced by a 15 kv electron beam, in $\text{CaTiO}_3\text{:Fe-Mo}$ (calcium titanate doped with iron and molybdenum) can be "erased" by visible radiation ($\approx 4500\text{\AA}$). The induced reflectance changes occur primarily in the 400-600 nm region, but trail off as far as 1000nm.

Gorog (ref. 18) describes the application of cathodochromic materials in image display devices. Here an image is formed by "writing" the information with an electron beam. Erasure is accomplished either by broad-band visible radiation, or thermally. Gorog, in his discussion of the mechanism of cathodochromic color switching, identifies valence shifts in defects or impurity ions (e.g., Fe^{+++} or Mo^{+5} ions in CaTiO_3).

Duncan, Faughnan, and Phillips (ref. 19) offer excellent discussions of photochromism and cathodochromism, explaining mechanisms of reversible color changes. Although they invoke a solid state description of the energy band structure of a dielectric material, they do not use it to full advantage. Nevertheless it is clear that photochromism and cathodochromism are processes not likely to be useful in camouflage applications because they produce a go/no-go condition. If the color response could be made dependent upon the intensity or some other controllable characteristic of the stimulus, then these processes could become useful. Understandably the authors were concerned about specific applications and did not look into the mechanisms of band broadening in color center formation. The latter might offer some hope of controlling color response in photochromic materials.

Maeda and Hayashi (ref. 20) discuss chromic effects based on dimerization of 2,4,5-triphenylimidazolyl, one dimer of which is photochromic and the other, piezochromic. Our interest in this paper stems mainly from the facts that the dimers are optically different, that the process is reversible, and that one dimer is piezochromic. The induced coloration in both the photodimer and the piezo-dimer disappears upon standing. In this case also the color change is a go/no-go change, even in the case of the piezochromism. Brothers and Lynch (ref. 3) investigated the effects of

pressure on the optical properties of several halide materials. The changes in optical properties induced by pressure occur as a result of the associated change in lattice constants, and the resulting shift in the fundamental optical absorption edge. From the data given, one can readily see that the production of color changes via pressure effects in inorganic dielectric materials would not be practical, for several reasons. First, the effect is much too small, of the order of $1-10 \times 10^{-6}$ eV/atm., which would produce a shift of 0.8-8 nm/10,000 psi. Second, the shift that occurs is in the position of the fundamental optical absorption edge; thus, even if the effect were large enough, it would produce strong absorption rather than selective reflection. It may be that organic compounds show greater pressure sensitivity, but no relevant information could be found.

The dependence of ultrasonic sound wave attenuation on direction through a magnetically ordered nematic liquid crystal was shown by Lord and Labes (ref. 21). Although the velocity change observed was very small, attenuation of sonic energy depends strongly on the angle between the direction of sound propagation and the direction of the aligning magnetic field in MBBA.

An article by Cherkashin (ref. 22) was at first thought to be useful, but upon close scrutiny we found that the reversal of dichroism they discuss would, if it could be induced practically, be another go/no-go effect spectrally, that is, there would likely not be a continuous adjustment over the visible region.

Our interest in the effects of strong electric fields on the electrical conductivity of polymeric materials led us to an article by Shilyaev and Gindin (ref. 23). We wanted mainly to determine the magnitude of the field strength required to increase electrical conductivity substantially. For the crystalline forms of the polymers polystyrene and polypropylene, it turns out to be $\sim 10^5$ eV/cm., and for

polyethylene terephthalate, $\sim 10^6$ eV/cm. Electrical properties, of course, arise from many of the same solid state properties governing optical absorption, especially in the visible and infrared region. The work by Novikov and co-workers (ref. 24) was studied for similar reasons; the voltage induced emission current and the effect of wavelength on it imply field effects which might be exploited. The spectra show a definite dependence on the nature of the applied voltage, whether constant or pulsed.

Numerous other articles (e.g., Refs. 25-36) covering a wide range of materials and mechanisms were reviewed, but no significant, additional or new information was found, because they deal with different aspects of the same effects.

2.4 Conclusions

An analysis of the literature indicates that there are many mechanisms through which color changes can be induced. Many are irreversible and most are discontinuous (go/no-go); but there are many which show promise in variable camouflage applications. Our judgement, however, is that only liquid crystals offer an immediate solution. In the long term, liquid crystals would also appear very competitive because of their controllability and considerable room for improvement.

It is abundantly clear that many effects exist which have potential applicability in active camouflage usages. Electroluminescence, for example, the basis for light emitting diodes used in hand-held electronic calculators, may be highly important, if the luminescence spectrum can be made variable and if the intensity can be reduced to that common to the reflected radiation intensity from vegetation and other real "backgrounds".

2.5 Liquid Crystal Chemistry

Molecules which possess a dipole and rod-like structure have an ability to orient parallel to each other. There are two major groups of orienting molecules: (1) the more rigid ones, which form nematic and smectic phases; and (2) the salts of fatty acids and phospholipids, which orient only to the extent that they interact with water.

The most widely applied liquid crystal structure is cholesteric. The cholesteric ester materials exhibit color due to twisting of the aligned molecules into a helix. The pitch of the helix determines the color. Normal nematic liquid crystal structures can also exhibit color:

(1) if the molecules possess dissymmetry which is the cause of optical activity, or

(2) if optically active additives are incorporated. An optically active compound possesses an asymmetric carbon to which four different substituents are attached in order to produce a color change the compound has to dissolve in the nematic material.

Another group of compounds, which exhibit color in two component structures, are polypeptides. Polypeptides are long-chain molecules which are intrinsically helical and optically active and they also possess some characteristics of nematic as well as lyotropic phases. They are lyotropic in the sense that solvent has to be present to induce color.

Our analyses of the literature and our consultation with Dr. Brown indicate that induced color changes can only be achieved using cholesteric liquid crystals. The nematic and smectic types do not show any variable color when stimulated but, in general, change from clear to cloudy when heat or voltage is applied. There are special cases, such as optically active nematic compounds and polypeptides with solvents, which exhibit color. The color changes, however, are not well documented and these systems are not as well defined as the cholesteric structures.

Table 3
EFFECT NOTED IN REFERENCES

LIQUID CRYSTAL
etc.

| MATERIAL | THERMAL | ELECTRIC | PRESSURE | MAGNETIC | ULTRASONIC | COMMENTS |
|---|---|--|----------|---|------------|---|
| C- Cholesteryl | | | | | | |
| Cholesteric: mixtures of cholesteryl chloride, nonanoate, and oleyl carbonate | | Voltage Effects Response time: 0.03 to 0.5 sec. | | | | Wavelength shifts Ref. 37 (Hayen) |
| Cholesteric: equal parts by wt.: cholesteryl benzoate, acetate, palmitate | | | | | | Optical: polarized light Ref. 38 (Ferguson) |
| Cholesteric: nonanoate with butyrates, crotonate, propionate | Chain length shifts temperature and sensitivity | Varying current on Mylar | | | | Chemical Structures and max scatter, also solvent vapor effect on color Ref. 39 (Ferguson) |
| P-methoxybenzylidene-p-cyanoaniline | Max orientation at 106°C | IR absorption vs d.c. field | | | | Ref. 40 (Neff) |
| Sodium palmitate | Mesophase line with only slightly temp. dependent | | | NMR: Width of mesomorphic Phase line indep. of bulk viscosity | | Ref. 41 (Lawson) |
| Lipid: monolaurin, pinacol, monopalmitin monostearin | | 50°C (5% water) 35-105°C (20% water) | | NMR: water held in solid state | | Liq. crystal range varies with water content Ref. 42 (Lawrence) |
| Alkory azobenzene, azoxybenzene | | Dielectric constants differ parallel and perpendicular | | | | Height of potential barrier method. Ref. 43 (Meier) |
| Potassium Oleate | | | | | | Transition concentration (electro-microscopy) Ref. 44 (Eins) |
| Potassium Oleate | | | | | | X-ray diffier and electromicroscopy Ref. 45 (Balmbra) |

Table 3 (Cont'd)

EFFECT NOTED IN REFERENCES

LIQUID CRYSTAL

etc.

| C- Cholesteryl MATERIAL | THERMAL | ELECTRIC | PRESSURE | MAGNETIC | ULTRASONIC | COMMENTS |
|---|--|----------------|----------|---|----------------------------|---|
| | | | | | | |
| Nematic Mesophase | +1°C per 2300 G field to orient parallel | | | Magnetic field parallel to axis causes no temperature change | | Ref. 46 (Miesowicz) |
| Cholesteric | Temperature dependent; minimum intensity of scattered light | d.c. up to 3kc | | | | Ref. 47 (Muller) |
| Nematic textures | | | | | | Marbled to threaded textures Ref. 48 (Sackmann) |
| P-azobenzonitrile | T>T _c incipient aggregation | | | | Ultrasonic absorp- tion | Adjacent domain transitions Ref. 49 (Edmonds) |
| MBBA N-(p-methoxybenzylidene)- p-n-butylaniline | 20-40° Nematic; very long thermal relaxation | | | Ultrasonic attenuation vs magnetic field: Anisotropy with alignment | | Ref. 50 (A. Lord) |
| MBBA and hydroxy substituted analogues | OH raises transi- tion m-alkoxy: no mesophase or no alkoxy: no meso- phase | | | | | Ref. 51 (Hirata) |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Table 3 (Cont'd)

EFFECT NOTED IN REFERENCES

LIQUID CRYSTAL
etc.

| C- Cholesteryl | | | | | |
|--|--|--|---|---------------------------|------------|
| MATERIAL | THERMAL | ELECTRIC | PRESSURE | MAGNETIC | ULTRASONIC |
| Azoxybenzene | | Forces between electrical dipoles; little effect on orientation (Solvents) | | Proton Magnetic Resonance | |
| Liquid Crystal Model: like melting polymers | | | | | |
| Amphiphilics: lecithin, bile salt, cholesterol | | | | NMR | |
| Azoxybenzene--benzoic acid with Acetylenic compounds | | Several acetylenic groups would be beneficial for conductivity | | NMR | |
| Cholesteryl n-Alkyl Carbonates | Low Temp. color band - reflection and transmission | | Mechanical Sensitive (high Temp) color band | | |
| Stigmasteryl Carbonates | | | | | |
| Polybenzyl-L-glutamate poly-v-ethyl-L-glutamate in ethyl acetate | Temp + concentration dependent (>30% conc) viscous gel | | | | |
| Most liquid crystals; Smectic-Nematic Transitions in higher C's | Smectic-nematic transition temp. defined by number of carbons | | | | |
| Cholesteryl Octanoate | Solid $\xrightarrow{110^\circ}$ Isotropic $\xleftarrow{69.5}$ $\xrightarrow{96.5}$ Smectic \rightarrow cholesteric | | | | |
| | | | | | |

COMMENTS
Ref. 52 (Saupe)

X-ray, electron, neutron: reflection

Ref. 53 (Hosemann)

Structures (L.C.) in water up to 45-50%
20.

Ref. 54 (Saall)

Ref. 55 (Englelt)

Length of alkyl chain determines temp, range of color bands, 56 (Elsger)

Synthesis: Only mixtures show cholesteric color.

Ref. 57 (Ohmann)

Colors: Cholesteric-lyotropic and nematic characteristics, 58 (Robinson)

Ref. 59 (Gray)

Few liq. crystals, are nematic only.

Ref. 60 (Gray)

Table 3 (Cont'd)

EFFECT NOTED IN REFERENCES

| LIQUID CRYSTAL etc. | | EFFECT NOTED IN REFERENCES | | | | | |
|------------------------|---|--|----------|----------|-----------------------|------------|--|
| C- Cholesteryl | | Thermal | Electric | Pressure | Magnetic | ULTRASONIC | COMMENTS |
| MATERIAL | Cholesteryl myristate | 70.2°C Solid→ ←smectic 77.6° smectic→ cholesteric | | | | | Enthalpy and entropy solvents Ref. 61 (Martire) |
| | | | | | | | |
| | Benzylideneanilines | <100° crystal→ ←nematic | | | | | Lateral dipoles Ref. 62 (Castellano) |
| | | | | | | | |
| | Poly(α-benzyl-L-glutamate) (polypeptide) | | | | Phase oriented NMR | | Casting and Swelling Ref. 63 (Samulski) |
| | | | | | | | |
| | Schiff's bases (anilines) | 80-120° transition with methyl to octadecyl | | | | | Ref. 64 (Dave I) |
| | Amino-benzoic acids | 90-200°C transi- tion methyl to octadecyl | | | | | Greater Temp stability Ref. 65 (Dave II) |
| | Carboxylic acid derivatives | 90-280°C lateral substituents | | | | | Polar - inc stability Size - dec stability Ref. 66 (Gray) |

Table 3 (cont'd)

EFFECT NOTED IN REFERENCES

LIQUID CRYSTAL
etc.

| C = Cholesteryl | THERMAL | ELECTRIC | PRESSURE | MAGNETIC | ULTRASONIC | COMMENTS |
|-------------------------------------|--|--|----------|---|------------|--|
| MATERIAL Cyclolanostan Palmitate | Melting violet - 64°C Cholesteric- isot. | | | | | Ref. 67 (Knapp) |
| Cholesteric | | | | Klystron: 1W (cw) at GHz (33°C) | | Microwave and electrical field to visual Ref. 68 (Setharis) |
| Anisole Cholesteryl Esters | 107 to 135°C | | | Spin-lattice relaxation 1 to 0.2 sec. | | Pretransition and hysteresis Ref. 69 (Rumyan) |
| Cholesteric | Spinning Theory | | | | | Ref. 70 (Leslie) |
| Aromatic Cinnamates | 79-160°C 2100 joules/mole 100% joules/mole | smectic to isotropic smectic C to A | | | | Adiabatic Calori- metry Ref. 71 (Arnold) |
| Various | 75 to 125°C transi- tions | Dielectric Changes | | Magnetic on dielectric | | Ref. 72 (Mark & Tobolsky) |
| Mesomorphic gels; copoly- mers | | | | | | Solvent effects Ref. 73 (Battaerd) |
| p-azoxyanisole phenyl radicals | | | | Electron Spin | | Degree of ordering Ref. 74 (Mobius) |
| | | | | | | |

Table 3 (Cont'd)

EFFECT NOTED IN REFERENCES

LIQUID CRYSTAL
etc.

| C- Cholesteryl | | | | | | |
|--|--------------------------------|----------|----------|-----------------|------------|--|
| MATERIAL | THERMAL | ELECTRIC | PRESSURE | MAGNETIC | ULTRASONIC | COMMENTS |
| Cholesteric | "Hot Spots" | | | | | Helix Structure Ref. 75 (Lawrence) |
| Naphthalene-Sulfonic | | | | | | Solvent: hydrophobic bonding Ref. 76 (Hand) |
| Potassium Oleate/Water | | | | | | Gel structure, elec- tromicroscopy Ref. 77 (Balmora) |
| Polyethylene | | | | | | Model of Liquid Ref. 78 (Hoseman) |
| Lyotropic: Lecithin, Bile salt, cholesterol | | | | NMR | | Water makes liquid crystal Ref. 79 (Small) |
| Azo compounds | Permanent electrical dipole | | | Proton magnetic | | Orientation in chlorosolvent Ref. 80 (Saupe) |
| | | | | | | |
| | | | | | | |
| | | | | | | |

The various classes of liquid crystals and their color characteristics are depicted in Figure 1.

Color changes can be induced in liquid crystals by changes in temperature, by electrical and magnetic fields, mechanical shear, ultrasonic waves and by molecular additives. The basis of color change is in all cases the change in the pitch of the helical arrangement of individual molecules. Whereas the smectic liquid crystal phase exhibits a highly ordered arrangement, within and between layers, an increase in temperature changes this arrangement to lesser ordered, threadlike (nematic) structures, while mechanical shear forces induce a helical twist to the nematic structure. In the cholesteric phase, as well as nematic-asymmetric structures and in polypeptide-solvent compositions, the pitch of the helical arrangement is increased by elevating the temperature and by applying electric, magnetic or ultrasonic fields. Shear and molecular additives have the same effect. In all cases a minimum value (transition temperature or threshold field level) has to be reached before the transition is noted. Some of the effects on liquid crystals are summarized in Table 3.

In the case of temperature-induced transitions, a color is achieved by mixing the liquid crystalline materials which have transition temperatures spanning the temperature range in which color is required. The quantitative ratio of two or three components yields the desired temperature range and also can expand it. This may also be true for electrical and other transition effects.

The transitions in nematic liquid crystals occur by a mechanism which is identical to the cholesteric transitions. The nematic threads are formed into a helical arrangement by the presence of asymmetric groups or additives. The pitch of these helical arrangements can be changed by the same techniques as in the cholesteric structures.

CLASSES OF LIQUID CRYSTALS

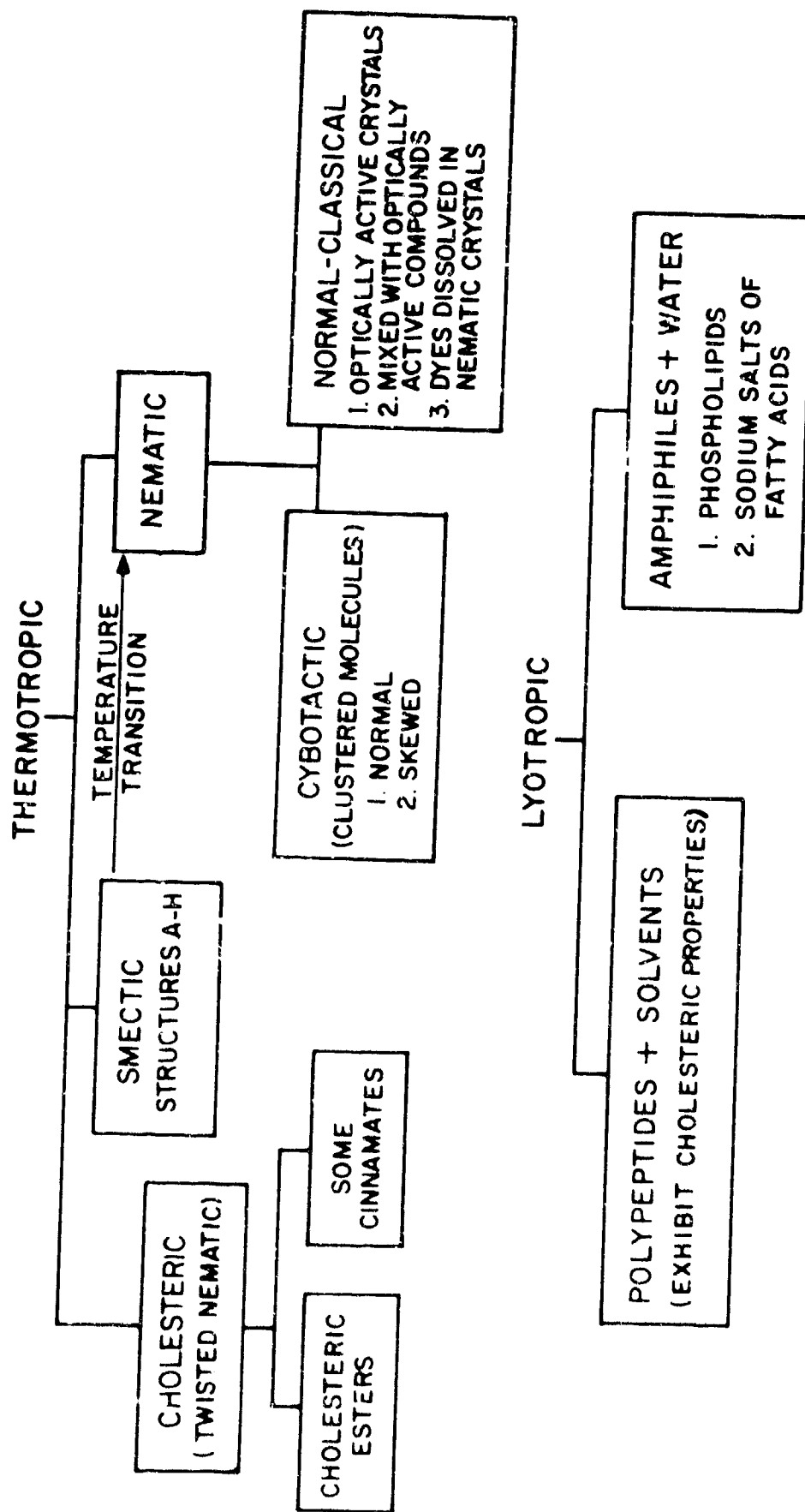


Fig. 1

The liquid crystalline phases which have lyotropic character require the presence of a solvent-additive for orientation. Laminal (layer) phases are reversibly induced by addition and removal of water in the amphiphiles. There is no direct evidence of helicity or color in the amphiphiles. However, polypeptides exhibit color when a specific solvent is added.

The polypeptide is a long-chain molecule which is itself helical, but very tightly coiled compared to the helical structures that exist in cholesteric phases. Polypeptide helicity depends upon solvent and temperature. The helix exists in non-interacting solvents (e.g., dioxane, dimethyl formamide and chloroform); it is randomized by solvents which break the hydrogen bonds of the peptide helix which exists in the solid state and is a rigid rod-like unit. When dioxane is added to the solid polypeptide, the individual helical units arrange in an overall helical configuration which is analogous to the cholesteric phase. The color changes are, however, not as well defined as in the cholesteric liquid crystals.

2.6 Symposium on Liquid Crystals

During the week of August 27-31, 1973, the Division of Colloid and Surface Chemistry of the American Chemical Society held a week-long symposium on Ordered Fluids and Liquid Crystals, in which 82 papers were presented. One of the authors attended most of the sessions and has reported the highlights of the sessions here.

Gruler et. al., stated that p-cyanobenzylidene p-octyloxybenzene, a compound similar to MBBA, exhibited a ferroelectric phase which in turn allowed the material to respond to a static magnetic field by distorting a splay-wave pattern. Dr. Petrie of Eastman Kodak in her paper cautioned against the association of the entropies of various mesomorphic transitions with those of optical

transitions. Professor McMillan of the University of Illinois discussed the molecular order and phase transitions of liquid crystals and attempted to explain certain properties in terms of order parameters, e.g., the lack of ferroelectric properties in the Smectic C mesophase.

A popular nematic material, poly- γ -benzyl-L-glutamate (PBLG), was studied also by DuPre' and Hammersmith, University of Louisville, Louisville, Kentucky. DuPre' showed that above a critical concentration PBLG forms a lyotropic liquid crystal of cholesteric structure in the presence of a sufficiently strong electric or magnetic field. This liquid crystal undergoes a mesomorphic phase transition to the nematic order. This transition under an applied field of 13 kilogauss takes several days to a week. DuPre' indicates that the structure is cholesteric in solvents such as CHCl_3 , CH_2Cl_2 , dioxane, m-cresol, and dimethyl formamide; in a mixture of 4:1 CH_2Cl_2 : Dioxane, however, it is nematic; while in benzene it takes on a smectic order.

Neubert and Carlino of the Liquid Crystal Institute, Kent State reported on a study of 4,4'-disubstituted phenyl benzoates, only the β -methyl compounds of which have mesomorphic phases. They show a curve of melting point ($^{\circ}\text{C}$) vs chain length of substituents, wherein the characteristic pattern of peaks and valleys is obtained: odd numbered substituent carbons resulting in low, and even numbers of them resulting in high, melting point temperatures.

Lee of Princeton compared his recently developed continuum theory of liquid crystals with the more prevalent Ericksen-Leslie theory, indicating differences in the ability to predict certain mass motion properties. In a paper, entitled "Induced Rotary Power in Ternary Mixtures of Liquid Crystals" by James Adams et. al. of Xerox, Webster, N.Y., the authors concluded that cholesteryl chloride (C-Cl) is a powerful color inducer, especially in the presence of a liquid crystal of opposite optical rotatory power. In this case the pitch of the ternary liquid crystal mixture (two cholesterics and one nematic) was found to be very non-linear with C-Cl con-

centration. Gerritsma and Van Zanten of the Philips Research Laboratories, Eindhoven, Netherlands, studied the electro-optical behavior of a mixture of 20% C-Cl and 80% C-oleyl-carbonate. They obtained a blue shift at an applied field strength of 20,000 V/cm in a 15 micron thick film, but indicated that the induced shift was inversely proportional to thickness. They discussed imperfect ordering as an explanation for lack of specularly in films under the influence of electric fields. Gibson and Pochan of Xerox, Rochester, N.Y. discussed steric effects of carbonyl groups and how these affect mesomorphic properties. They displayed a correlation of inverse-pitch vs structure.

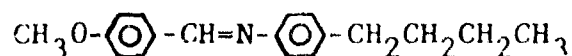
Several papers dealt with the synthesis of homologous series of various liquid crystal systems, others with descriptions of mesophases and their individual temperature regimes, and still others provided structure property relationships.

2.7 Consultation with Dr. G.H. Brown

On September 28, 1973, three of the authors visited with Dr. Glenn H. Brown, an internationally known and recognized expert in liquid crystal technology, and Director of the Liquid Crystal Institute of Kent State University, Kent, Ohio. The discussions were very informative. After being briefed on the objectives of this program, Dr. Brown gave some background on and the applicable theory of liquid crystals. A key point in his discussion was that, while the liquid crystal approach in general holds merit, only cholesteric liquid crystals will exhibit a continuous reversible color change under the influence of an external stimulus; other liquid crystals have only go/no-go properties.

The most commonly used liquid crystals are MBBA,* a nematic liquid crystal, and a mixture of cholesteryl nonanoate and cholesteryl-oleyl-carbonate. To the latter mixture is often added cholesteryl chloride, an optically active compound which greatly enhances the hue and color response and affects the colorplay.

*MBBA = N-(p-methoxybenzylidene)-p-n-butylaniline



Some cholesteric compounds also respond to other external stimuli such as magnetic and electric fields, mechanical shear, ultrasonic shear and molecular additives.

Dr. Brown recommended that we experiment with the mixture:

| | |
|------------------------------------|-----|
| Cholesteryl nonanoate | 47% |
| Cholesteryl oleyl-carbonate | 47% |
| Cholesteryl benzoate (or chloride) | 6% |

These materials, he pointed out, are the ones used commercially in liquid crystal products. For practical purposes he suggested that an ultraviolet absorber be utilized in liquid crystal systems in order to extend the useful shelf life, noting that in some cases shelf life is limited because of hydrolysis, action of impurities, oxidation, ultraviolet photochemistry, etc., and that an ultraviolet absorber could improve shelf life from about 4000 hours to better than 16,000 hours.

The origin and theory of color change in cholesteric liquid crystals was discussed at some length. Basically, the color of such crystals results from diffraction of light by the individual molecular planes, the distance between which (the pitch) is of the order of the wavelength diffracted. The actual color, however, appears different to an observer depending upon the angle of viewing. Temperature and other external stimuli change the pitch distance and thus the diffracted light pattern. The pitch actually changes as a result of the twisting or untwisting of the molecular plane orientation - depending in this case upon the direction of the stimulus.

The diffracted light pattern from a liquid crystal is of little utility in a camouflage application because of the specularly problem - color being a function of angle of viewing. The specularly problem can be minimized if the liquid crystals can be randomized in orientation directions, in which case only the dominant order defined by pitch distance would be observed.

3. EXPERIMENTAL ACTIVITIES

A wide variety of liquid crystals, compounds, devices and related materials were ordered and tested in this program. Several materials exhibit non-uniform or otherwise undesirable color change properties. When the colorplay - a term used to indicate the temperature (or other stimulus) range over which the full spectrum of colors is observed - is very small, the color is extremely sensitive to even the slightest fluctuations in temperature.

A testing scheme was set up to attain a quick-look capability to determine whether a subject material responds to temperature (in a reasonable temperature range), to an electric field, to a magnetic field, and to an applied strain. An apparatus to test the response to induced electric field was also constructed.

In all of the experiments to date it is obvious that a full range of visible colors can be generated in some liquid crystals by external stimuli. A 50-50 mixture of cholesteryl chloride and cholesteryl nonanoate has been used as a crude reference material since its colorplay and response times are discussed in the literature. These two components quite probably are the ones most frequently used in commercial applications. The initial experiments were carried out mainly to determine colorplay, electric field effects, response times, and practical difficulties in performing colorplay experiments.

3.1 Liquid Crystal Mixtures - Syntheses and Properties

3.1.1 Introduction

The objective of this study was to lower the enantiotropic range of the tri-mixture cholesteryl nonanoate (C-N), cholesteryl chloride (C-Cl) and cholesteryl-oleyl-carbonate (C-O-C) to a practical temperature range centered around 50°C (Ref. 81), and to broaden

the colorplay of this mixture to as much as 100° . It is assumed that the thermotropic color response in the mesophase will stabilize. Also, when this transformation can be accomplished thermally, it may be possible that other methods can be applied to induce a color response with little hindrance from such environmental effects as light, wind, hot spots, etc.

The principle of mix-melting point was used to effect the lowering of the enantiotropic range. Known methods of expanding the enantiotropic range include varying the mount of C-Cl, and using liquid crystal compounds that have a broader mesomorphic range and/or increased color display than C-Cl, such as cholesteryl acetate (C-Ac) and cholesteryl propionate (refs., 37, 82, 83). In another method, doping the liquid crystal with non-liquid crystalline materials can induce the homeotropic orientation in the liquid crystal; such additives as lecithin, polyamide resins, quaternary ammonium salts, etc. (ref. 84) are good examples. Thus, experiments were designed and carried out in the manner described below in order to achieve a broad colorplay in the temperature range of $45-55^{\circ}\text{C}$.

3.1.2 Experimental

The liquid crystals were obtained from the Eastman Chemical Co. and the Aldrich Chemical Co. They had the following mesomorphic ranges: C-N, ($78-98^{\circ}\text{C}$); C-Cl, ($98-99^{\circ}\text{C}$); C-O-C, (room temperature); and C-Ac ($114-116^{\circ}\text{C}$) - all of which were used without further purification. The additives used were laboratory reagent grade and were also used without additional purification.

The heating apparatus was constructed from a 1x5-inch silicone rubber heating mat (Cole Palmer Co., Watlow 01005001, 120V, 25 watts). This mat was connected to a laboratory variac which controlled the heating rate. The temperature was measured with a Leeds and Northrup potentiometer which was connected to the heating mat through a 3 mil bare iron-constantan thermocouple wire (Omega Engineering, Inc.).

The experiments were carried out by weighing out various proportions of the tri-mixture components into a 3 dram vial. Then the mixture was heated to its isotropic melt point. This melt was placed on a black-backed plastic sheet (Edmund Scientific Co. No. 500132-1) with an applicator stick and sandwiched between two glass slides. The slides were then placed on the silicone rubber heating mat and heating commenced. The ambient temperature and the corresponding color responses of the liquid crystal mixtures were measured by means of the unaided eye and by microscopic means. Observations of color vs temperature were recorded.

3.1.3 Results and Discussions

3.1.3.1 Lowering of the Tri-Mixture Temperature to a Workable Temperature Near 50°C

The workable temperature sought for the practical purpose here is around 50°C. In order to obtain this temperature, the principle of mix-melting point was applied, a standard procedure used by organic chemists in the identification of organic compounds and/or their purity. This workable temperature range was readily obtained by keeping the quantity ratio of C-Cl to C-O-C constant and by varying C-N concentration, - as if by increasing or decreasing impurities in an otherwise pure compound. The basic mixture was prepared according to the following percentages: C-N : C-Cl : C-O-C = 84.3 : 3.6 : 12.1; it has an enantiotropic range of 49°C (red) to 54°C (blue), as shown in table 4, (exp. no. 17). This mixture, however, did not broaden the colorplay ($\Delta t = 5^\circ$) and did not give stable color response in this range. Experiment number 16, which was a similar percentage except that the relative quantities of C-Cl and C-O-C have been reversed, shows the same relative workable range (43-54°C) as exp. no. 17 but with broader enantiotropic range ($\Delta t = 11^\circ$); it also shows excellent color stability. In exp. no. 22, however, the enantiotropic range was higher than the desired range but the extent of the range, the colorplay, was 18°C. The mesophase color response was very poor as will be explained subsequently. Also, a di-mixture, C-N : C-Cl = 90 : 10 (exp. no. 4) gave a workable temperature of 46 to 58°C ($\Delta t = 12^\circ$) and a stable color response.

Table 4

COLORPLAY IN

CHOLESTERYL CHLORIDE CONTAINING TRI-MIXTURES

| No. | Tri-mixture Wt. % | | | Color Response Temperature, °C | | Comments |
|-----|-------------------|------|-------|--------------------------------|------|---|
| | C-N | C-CL | C-O-C | Red | Blue | |
| 1 | 100 | - | - | 82 | 88 | 6 Fast colorplay change; cooling: 77°-green, 73°-red |
| 2 | - | 100 | - | - | 24 | 0 r.t.-Blue, no colorplay |
| 3 | - | - | 100 | - | 24 | 0 r.t.-Blue |
| 4 | 90 | 10 | 0 | 46 | 58 | 12 46-48°C-red |
| 5 | 87.5 | 12.5 | - | 37 | 50 | 13 Slow colorplay change; 47°-green (heating); Cooling 52°-blue, 43°-green, 39°-complete green yellow appears, 37-33° red |
| 6 | 70 | 30 | - | - | 25 | - r.t.-blue |
| 7 | 57.8 | 42.2 | - | 24 | - | 0 r.t.-red; no colorplay on heating to 101°C |
| 8 | 87.6 | - | 12.7 | 60 | 66 | 6 Tan colored mixture; no colorplay |
| 9 | - | 50 | 50 | - | - | 0 r.t.-Multi-colored, mostly red; pressure and shear sensitive - green when sheared |
| 10 | 33.3 | 33.3 | 33.3 | 45 | - | 0 Tan colored mix; r.t.-dark red; no colorplay on heating to 95°C |
| 11 | 13.8 | 75.6 | 10.6 | 25 | - | 0 r.t.-greenish blue |
| 12 | 63.6 | 27.3 | 9.1 | - | 24 | 0 r.t.-green; pressure changes green to blue; fast colorplay |
| 13 | 71.4 | 21.4 | 7.2 | 24 | 86 | 62 |

Table 4 (Cont'd)
CHOLESTERYL CHLORIDE CONTAINING TRI-MIXTURES

| No. | Tri-mixture Wt. % | | | Color Response Temperature, °C | | Comments | |
|-----|-------------------|------|-------|--------------------------------|---------|----------|--|
| | C-N | C-CL | C-O-C | Red | Blue Δt | | |
| 14 | 73.8 | 15.7 | 10.5 | - | 24 | 0 | r.t.-purplish-blue |
| 15 | 77.8 | 11.2 | 11.0 | 29.5 | 37 | 7.5 | r.t.-light multi color |
| 16 | 83.7 | 11.7 | 5.6 | 43 | 54 | 11 | 48°-(green); 54°-blue; 65°-complete blue; on cooling: 67°-blue; 41°-green, 39°-violet-yellow, 37°-red, 35°-brown |
| 17 | 84.3 | 11.7 | 5.6 | 49 | 54 | 5 | Rapid colorplay |
| 18 | 88.1 | 2.8 | 9.1 | 57 | 62 | 5 | Rapid colorplay |
| 19 | 93.8 | 1.4 | 4.8 | 64 | 65.5 | 1.5 | Rapid colorplay |
| 20 | 96.8 | 0.7 | 2.5 | 69 | 71 | 2 | Rapid colorplay |
| 21 | 97.4 | 0.6 | 2.0 | 70 | 74 | 4 | Rapid colorplay |
| 22 | 97.7 | 1.7 | 0.5 | 77 | 95 | 18 | Limited colorplay: a narrow band of green-yellow-red moves across sheet rapidly till completely blue |

3.1.3.2 Stabilizing the Color Play

3.1.3.2.1 Cholesteryl Chloride

Although broader enantiotropic ranges were obtained within the desired workable temperature range, the colorplay was not stable in some of the ranges. Thus, further studies were made in stabilizing the colorplay.

It is known that by varying the amount of C-Cl of this tri-mixture, it will shift the color response and temperature (Refs. 37 and 83). However, there seems to be a limit to the amount of C-Cl that could be varied as shown in Table 4, exp. nos. 5, 7 and 10. Percentages above 30% tend to show a strong red color. The red color that shows at 42.2% and 75.6% interestingly showed no color display on heating or cooling. Increasing the amount of C-O-C will tend to give blue or multicolored crystals at room temperature as indicated in exp. nos. 13, 14, 15 and 17. Equivalent amounts of each (exp. nos. 9, 10 and 15) show no color display or multicolored crystals at room temperature.

Expanding the enantiotropic range of the tri-mixture was possible with the following concentrations: C-N : C-Cl : C-O-C
83.7 : 11.7 : 5.6 (exp. no. 16) and 97.7 : 1.7 : 0.5 (exp. no. 22). The red to blue ranges were expanded 11C° and 18C°, respectively. The colorplay, however, does not stabilize uniformly as assumed. As an example, in exp. no. 22, a colorplay of green, yellow and red forms a narrow band followed by the blue as soon as it appears and moves across the sheet as a narrow band till the sheet becomes completely blue. The same phenomenon occurred during cooling. In the former, exp. no. 16, the colors were more pronounced and stable ($\Delta t = 2C^\circ$). On heating, red was difficult to detect: 48°C-green, 54°C-blue and completely blue at 65°C. On cooling from 65°C which shows blue, green appeared at 41°C, violet and yellow tinge at 39°C, red at 37°C and finally brown at 35°C. Although the enantiotropic range is greater in exp. no. 22, the colorplay range and stability is superior in exp. no. 16.

As already mentioned, the di-mixtures of 87.5% C-N and 12.5% C-Cl (exp. no. 5) showed promising enantiotropic range and mesophase colorplay stability. This mixture shows: (on heating) red at 37°C, green at 47°C and completely blue at 50°C; (on cooling from 53°C) blue, blue-green at 43°C and completely green at 39°C ($\Delta t=14^\circ$), (yellow appeared and rapidly shifted to red at 37°C), and completely dark red at 33°C. Also, exp. no. 4 transformed similarly as exp. no. 5 which has the workable temperature range sought.

3.1.3.2.2 Cholesteryl Acetate

Despite the sufficient expansion of the workable temperature in exp. no. 4, 16 and 22 of the C-Cl containing tri-mixture, the color-green yellow and brown were less stable during the heating cycle. Thus, it was decided to replace C-Cl with C-Ac to add colors and improve their stability. It has been shown that C-Ac or cholesteryl propionate (C-Pr), having a spectrum of violet, blue green, yellow and orange, shows more color response and wider enantiotropic range with C-N (refs. 37, 82 and 85) than with C-Cl. An 80% C-N and 20% C-Ac gives about a 40°C colorplay with colors yellow, green and blue (ref. 37) and the same percentage of C-Cl results in a 30°C range with a greenish-yellow color. The results of these experiments are summarized in Table 5.

As with C-Cl, C-Ac itself does not show visible color display on heating or cooling. Also the 50% mixtures of C-Cl : C-O-C and of C-Ac : C-O-C do not show any color display. The equivalent mixture of both tri-mixtures again showed no color display except that it was light blue at room temperature. The increase in C-Ac (exp. no. 8 and 11) showed either no color display or multicolored at room temperature. An interesting observation was made in the former mixture in that on heating there was no color display but, on cooling, mixed color was observed. Thus, C-Ac has some optical properties similar to those of C-Cl when mixed with C-N as shown in table 5.

Table 5

COLORPLAY IN

CHOLESTERYL ACETATE CONTAINING TRI-MIXTURES

| E X P No. | Tri-Mixture Wt. % | | | Color Response Temperature, °C | | Comment |
|--------------------|-------------------|------|-------|-----------------------------------|------|---|
| | C-N | C-Ac | C-Q-C | Red | Blue | |
| 1 | 100 | - | - | 82 | 88 | 6 Fast colorplay change; cooling: 77°-green, 73°-red |
| 2 | - | 100 | - | - | - | 0 No colorplay |
| 3 | - | - | 100 | - | 24 | 0 r.t.-blue |
| 4 | 87.5 | 12.5 | - | 48 | 60 | 12 48°-red-green, 50°-red, 60°-blue; on cooling: 62°-blue, 54°-blue-green, 48°-red-green-blue, 41°-completely red |
| 5 | 87.6 | - | 12.7 | 60 | 66 | 6 On cooling: 66°-blue, 58°-green with red border, 52°-red |
| 6 | - | 50 | 50 | - | - | 0 No colorplay |
| 7 | 33.3 | 33.2 | 33.4 | - | 25 | 0 r.t.-light blue |
| 8 | 12.9 | 86.9 | 0.2 | - | 86 | 0 No colorplay when heated to 177°C On cooling: 86°-blue-red, 60°-reddish-green |
| 9 | 84.3 | 3.6 | 12.1 | 52 | 58 | 6 Cooling: 52°-reddish green, 47-43°-red, 43°-blue |
| 10 | 76.8 | 11.6 | 11.6 | 25 | 39 | 14 r.t.-dark red (or violet); pressure sensitive; 25°-complete red, at 39°-complete blue; on cooling: 35°-blue 27°-blue green, 126°-green-blue-red, 24°-blue-green-red-yellow |
| 11 | 82.3 | 16.2 | 1.5 | 24 | - | 0 r.t.-red, green, blue, mostly red. |

The workable enantiotropic range of about 50C° was obtained with the di-mixture of 87.5% C-N and 12.5% C-Ac and with the tri-mixture C-N : C-Ac : C-O-C = 84.3 : 3.6 : 12.1 (exp. no. 9) with a colorplay of 12 and 14C°, respectively. They contained less stable monochromes than with C-Cl. The colors did not blend as well as C-Cl tri-mixtures.

3.1.3.2.3 Additives

It is well known that solutions of gases, liquids, and solids in the cholesteric liquid crystal can affect its structure so that one or more of the optical properties are permanently or temporarily changed (ref. 84). For our purposes the solids were chosen in an attempt to broaden the enantiotropic range and to stabilize the colors of the C-Cl containing tri-mixture, di-mixture and mono-mixtures as shown in Table 6.

Some of the solids that had been added to the liquid crystals (C-N : C-pr di-mixtures) (ref. 37) are fatty acids, lecithin, polyamide resins, quaternary ammonium salts and l-menthol (ref. 84).

Triton X-100 which has a cloud point temperature of 66°C was used in order to find some relationship in the changes of optical properties. Triton X-100 did not affect the optical properties in any way. Paraffin wax had no effect on the optical properties of liquid crystals. Swift's protein colloid depressed the enantiotropic range, and at 11.6% it showed no colorplay. Also, the cholesteric effect became irreversible, probably due to hardening of the colloid. With OI-650, a polysiloxane, the enantiotropic range and the colorplay were depressed (exp. no. 11), at 12% OI-650, it became incompatible with the liquid crystal. Cab-O-Sil at 4.2% depressed the enantiotropic range. Solute SE-30 at 10.9% showed partial incompatibility; however, the color display occurred in steps from section to section (exp. no. 13), as if it had isolated the crystals from each other. Dexil 200 showed compatibility, but without any colorplay.

Table 6

EFFECTS OF ADDITIVES ON THE COLORPLAY OF LIQUID CRYSTAL MIXTURES

| E X P No. | Tri-mixture Wt. % | | | Additives Name | Am't | Color Response Temperature, °C | | | Comment |
|--------------------|-------------------|------|-------|--------------------------|---------|-----------------------------------|------|------------|--|
| | C-N | C-CI | C-O-C | | | Red | Blue | Δt | |
| 1 | 71.4 | 21.4 | 7.2 | Triton X100 | 1 drop | 52 | 58 | 6 | no colorplay on 1st heating; 2nd heating showed color |
| 2 | 90 | 10 | - | " | 3 drops | 48 | 52 | 4 | 51°-green; very little change from w/o additive |
| 3 | 70 | 30 | - | " | 5 drops | - | 25 | 0 | r.t.-Blue; no change from w/o additive |
| 4 | 71.4 | 21.4 | 7.2 | Paraffin Wax | 2 mg | - | - | 0 | no colorplay |
| 5 | 90 | 10 | - | " | 4 mg | 52 | 58 | 6 | Same as Triton X100 |
| 6 | 90 | 10 | - | " | 13. mg | 48 | 52 | 4 | Lowered temp & color shifted |
| 7 | 72.8 | 10.9 | - | Swift Protein colloid | 15.8% | 39 | 48.5 | 9.5 | Irreversible change; depressed temp. range |
| 8 | 85.7 | - | - | " | 13.3% | 74 | 76 | 2 | Glue-like mass; lower temp.; shifted color |
| 9 | - | 88.4 | - | " | 11.6% | - | - | 0 | Incompatible, no color dis- play |
| 10 | 83.9 | 9.9 | - | OI-650 | 6.2% | 54 | 60 | 6 | Compared exp. No. 5 Table 1: increased color play range; narrowed the mesophase temp. range |
| 11 | 83.9 | 9.9 | - | " | 12.7% | - | - | - | Incompatible |
| 12 | 85.3 | 18.6 | - | Cab-O-Sil | 4.2% | 52 | 54 | 2 | Compared Exp. No. 10 above; Mesophase range decreased |
| 13 | 81.4 | 7.7 | - | SE-30 | 10.9% | 48 | 58 | 10 | Incompatible color display in steps or section at a time |
| 14 | 81.4 | 7.7 | - | Dexil 200 | 1 drop | - | - | 0 | No colorplay |

3.1.4 Conclusions

In C-N : C-Cl : C-O-C mixtures, varying the C-N concentration produces a shift in the workable temperature range and in the colorplay. Although it appears that these two variables are not linearly dependent upon the concentration of any individual component, the workable temperature range and colorplay of C-N : C-Cl : C-O-C mixtures can be adjusted by controlling their compositions. Di-mixtures likewise can be adjusted in composition to produce a wide range of these properties. The use of additives also shows some promise toward adjustment of these properties, but considerably more effort is required to develop this approach to the point where it would be as feasible as the di-mixture or tri-mixture approaches.

4. DEMONSTRATION MODEL

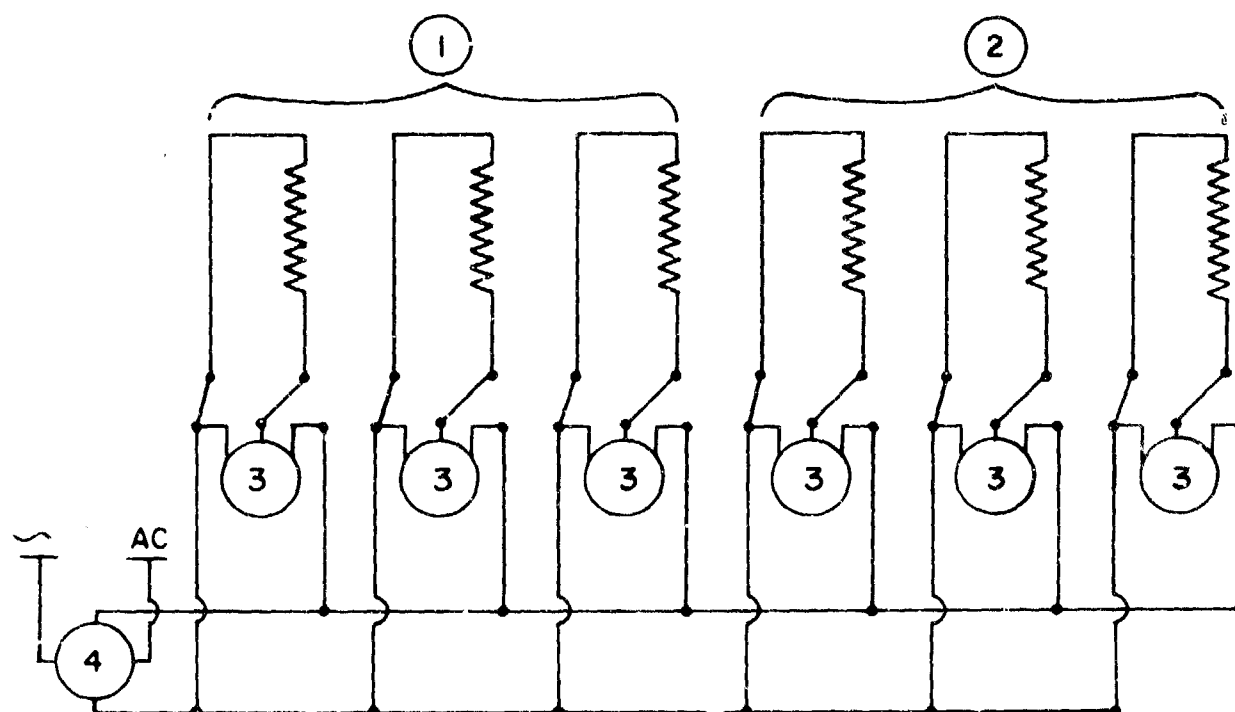
4.1 Temperature Controlled Color Panel

In an effort to determine the color spectrum exhibited by commercially available liquid crystal sheets, a temperature controlled color panel board was fabricated. This board consists of five 1.0 in. X 5.0-in. silicone rubber heating mats (Watlow 25 watt heater) bonded to a Masonite board. The heaters are powered individually through rheostats, thus making it possible to control the temperature of each. A 1.0-in. X 4.0-in. X 0.020-in. aluminum plate was bonded to each heater face surface utilizing an RTV silicone adhesive (G.E. RTV 108). The aluminum plates present a smooth, uniform surface to which liquid crystal sheets are attached, and also serve to distribute the heat uniformly. Liquid crystal sheets (Edmund Scientific, No. 71142, 30-36°C) were cut into 1.0 in. X 4.0-in. strips and attached to the aluminum plates by means of a double faced pressure sensitive tape. In this manner intimate contact between the heated surface and the liquid crystal sheet was attained.

The color panel board was used to elicit five colors from a 30-36°C range liquid crystal sheet. The five colors were generated by holding each strip at a different temperature within the 30-36°C range. They were then used as references in formulating oil paints for painting background scenes for the camouflage model tank.

4.2 Fabrication of a Heating Shroud for a Model Tank

A plastic model of an M-60 tank was selected for use in preparing a portable camouflage mock-up display. Because of the varied geometry of the tank, it was not feasible to apply liquid crystal sheet material directly on its surface. For this reason a shroud, which fits over the model tank, was fabricated from sheet metal. The shroud presents flat surfaces to which liquid crystal sheet material can be applied in this case by means of double faced pressure sensitive tape. In addition to presenting a surface to



1. GRAPHITED AREAS IN
BODY SHROUD
2. GRAPHITED AREAS IN
TURRET SHROUD

3. OHMITE 25 WATT, MODEL H
1000 OHM RHEOSTATS
4. 600 WATT VARIABLE
TRANSFORMER

Fig. 2 SCHEMATIC OF TANK SHROUD HEATING CIRCUITRY

which the liquid crystal sheet can be adhered, the shroud also serves as a constant temperature heat source necessary to effect a color change in the temperature sensitive liquid crystal sheet affixed to it.

Two such shrouds were fabricated: one to fit over the body of the tank, and the other, to fit over the turret. The metal shrouds were insulated (electrically) by coating with an epoxy paint; and, in addition, the inner surfaces of the coated shrouds were lined with canvas. To facilitate heating of the shrouds, area heating elements were prepared utilizing a colloidal graphite dispersion (Acheson Colloids Co. Dag Dispersion No. 154.) The liquid graphite dispersion was painted on the canvas linings in three electrically distinct areas, thus obtaining three separate circuits in each shroud. By controlling the voltage supplied to each circuit a specific temperature gradient in the heated area is obtained. The graphite coating thicknesses were built up in layers until each circuit exhibited a resistance of ~1000-1500 ohms. At this resistance level the graphite areas heat up at low voltage input (30-50VAC or DC).

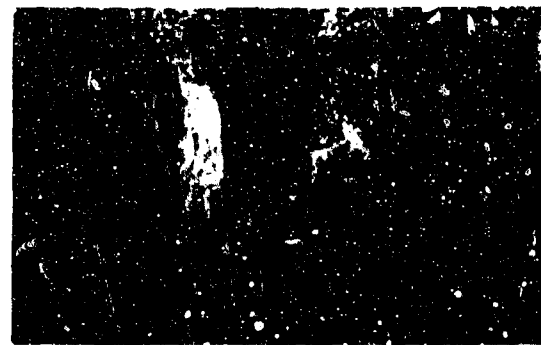
The three graphite areas of each shroud were connected to individual rheostats (Ohmite, 25 watt model H) mounted on a control panel. The six rheostats in turn are powered by means of a main rheostat (600 W. variable transformer). Thus, the power supplied to the graphite heater areas can be controlled individually and, allows various temperatures to be attained which correspond to desired colors. A schematic of the circuitry is shown in Fig. 2.

4.3 Demonstration Model

Two background scenarios were constructed to be used with the model tank in the demonstration of potential camouflage capability. One depicts a wooded scene and is predominantly made up of greens and browns and various shades of each. The other shows a desert or arid region and is predominantly brown and sand colored. When the model tank is placed in front of these scenarios and the rheostats are turned to appropriate settings, the color of the tank blends with the colors in the respective background scenarios. Figure 3



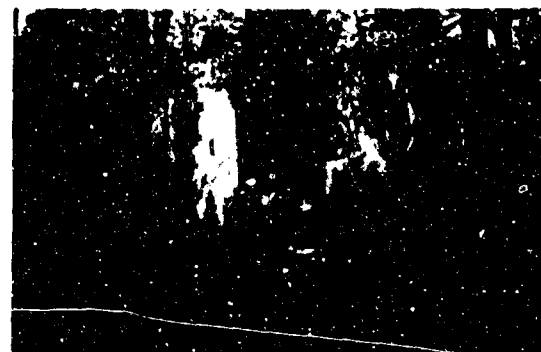
Time = 0 Seconds



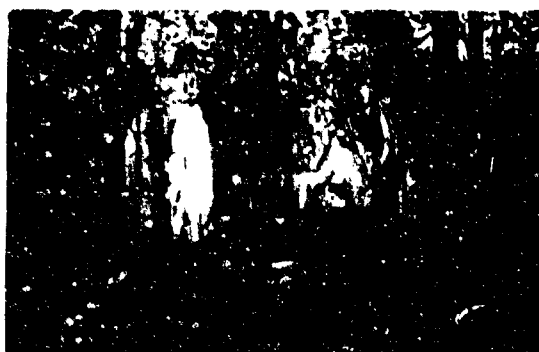
Time = 60 Seconds



Time = 20 Seconds



Time = 80 Seconds



Time = 40 Seconds

Figure 3

MODEL TANK IN SIMULATED DYNAMIC CAMOUFLAGE
PROGRESSIVE STAGES OF COLOR ADAPTABILITY

shows color photographs of the tank in front of the scenario of the wooded scene; the frames, taken at 20 second intervals, show the tank model as it progressively changes from all black at $t=0$ seconds to a camouflaged pattern of brown, green and blue-green at $t=80$ seconds. The rate of response of this camouflage system depends upon the applied voltage. In this case the actual settings of voltages in the various circuits were established on the basis of a desired color pattern. Faster or slower responses, of course, are possible by adjusting the driving voltages upward or downward, but would result in an overshoot or undershoot, respectively, of the desired color and/or color pattern. As the photographs show, the (black) color of the tank and the color patterns of the background initially contrast rather sharply. As voltage is applied, the contrast obviously is reduced, until at $t=80$ seconds, the color match is reasonably good. This demonstration shows that this approach to the vehicular camouflage problem has merit. The fact that a zero contrast over the entire scene could not be realized reflects the non-ideality of the commercial liquid crystal system employed as well as the difficulty in achieving realistic geometries in terms of viewer-tank-background relationships. The decreased fidelity of reproduced color photography, of course, also makes the evaluation more subjective. The considerable reduction in contrast, nevertheless, is evident and this alone indicates the merit of this approach.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

Liquid crystals, because of their advanced technology, possess an obvious advantage over most other conceptual possibilities: they do sustain continuous, reversible color changes under the influence of a controllable, external stimulus. A practical appraisal, however, suggests that many serious problems associated with their effective use must be resolved. We did not find the ideal liquid crystal system, although we are reasonably certain that one exists or could be compounded. The principal problem will actually be not one of finding a material or system of materials with ideal properties but one of satisfying the practical requirements of the program. The work accomplished in fabricating the canvas camouflage systems proved frustrating because of failures of many of the candidate systems. The flexible canvas system used on the model would not meet all of the practical requirements, but it was developed with these requirements in mind. In the case of durability, for example, this system as presently fabricated would have limited life, but by applying tough, transparent weather resistant coatings to the external surface, the system's durability could be greatly increased. Also of major concern was that the electrical continuity of the graphite coating would be lost after the canvas system is folded over on itself (in the same manner as folding a blanket for storage). Repeated flexures of this kind, however, had very little effect on electrical continuity. Hence, we believe that the durability of this particular system will not be a major problem.

Economics and producibility are inter-related questions, and difficult at this time to assess. All of the materials used, however, are commercially available. Thus, apart from the questions of availability and cost of the liquid crystal materials, the remaining question has to do with producibility - the feasibility of the process. It is our opinion that each of the fabrication steps

are easily adaptable to large scale manufacturing operations, including the deposition of a graphite film on the canvas.

Because this system is highly flexible and reasonably lightweight, its installation on vehicles would be rather easily facilitated. Tying its electrical circuitry into a vehicle's electrical energy system likewise could be accomplished without major interference with that source. The controls for the camouflage system would remain separate from, and independent of, any of the vehicle's control centers and, therefore, this concept of a camouflage system tends to have the least impact on the normal operation of combat vehicles.

Commercially available liquid crystal systems lack the desired colorplay, but it seems probable that liquid crystals meeting the requirements of this program could be developed, as we have shown. The principal difficulty with current commercially available liquid crystal systems is that few display the full spectrum of colors from far red to the deep violet regions. Since natural backgrounds rarely contain colors in the blue-violet region, and since this is the region in which liquid crystals usually are color-deficient, the requirement for color in this region could be compromised with little penalty to performance and with an increased likelihood of developing a workable liquid crystal composition. We believe that a controllably reversible camouflage system with excellent potential for full scale development has been demonstrated. The present system demonstrates that this approach has merit, even though it has many short-comings and many developmental hurdles to overcome. The fact that this system was reduced to a model on the basis of available technology lends substantial credence to our contention that a practical system based on thermally driven liquid crystals lies within our reach.

Our observations and analyses also indicate that the liquid crystal eventually developed or chosen should be encapsulated in a thin layer of a protective material to form "particles" of the order of 500 nm diameter. This process has several important advantages. It maximizes light scattering and thus reflectance, minimizes both gloss and specularly by randomizing the crystal axis orientations, and, if the encapsulant is chosen with ultraviolet radiation protection in mind, the shelf life of the product can be greatly increased. Since light scattering effectiveness depends strongly upon the ratio of particle size to wavelength the particle size should be adjusted for maximum reflectance in the 500-700 nm region. Minimizing gloss and specularity is critical. The chemistry of emulsions and of latices has advanced considerably in the past 20 years, and hence there should be no serious problem in the task of developing an adequate latex system.

Finally, regarding the potential of other possible variable camouflage systems, we should point out that nearly every such system will require some applied research and development to advance its technological position sufficiently to be useful. Light sources, for example, may find widespread use, if both the spectrum and intensity of induced luminescence can be varied. Utilization of biochemical systems is the furthest away of any approach, because of the huge knowledge gap and the technological difficulty involved in its adaptation. The mechanisms of color changes in various animate species have received far too little attention (Ref's 91-94) in terms of applicability to variable camouflage systems. The present state-of-the-art in our estimation is more than adequate to reduce to practical, working systems the concepts of electrically-driven liquid crystals, light emitting devices (with variable spectrum and intensity), and combinations of these and mechanical devices (shades, shutters, etc.). In any system involving liquid crystals, however, there will be the need to encapsulate them for protection and for assuring random orientations.

5.2 Recommendations

As we have stated, the liquid crystal approach to variable camouflage has demonstrable merit, and other concepts also have considerable potential for this application. Consequently, it is our considered opinion that, as a logical continuation of the work described in this report, the following R&D work should be accomplished:

- Liquid crystal technology - applied research programs to obtain: 1). liquid crystals with a full visible color spectrum, a 10-14C° colorplay, and 40-50°C onset temperature; 2) liquid crystals with a full visible color spectrum, a color play of 100Vdc in films of 5-10 micron thickness; 3) a protective encapsulant compatible with durable latex vehicles and an encapsulating process leading to the production of 0.5-0.7 micron "particles".
- Electroluminescent Devices - fundamental research in the physics of electrically stimulated light emission, followed by applied research to develop materials whose luminescence response can be varied spectrally and in intensity by electrical means; and the investigation of the effects of multiple, concurrently acting stimuli (e.g. pressure and electric fields) on the spectrum and intensity of induced luminescence.
- Lyotropic Systems - applied research to determine basic feasibility of lyotropic systems and to identify combinations of liquid crystals and solvents which exhibit color; and development of mechanical systems for application of osmotic pressure in lyotropic systems.
- Bio Systems - fundamental research into the biochemical mechanisms and physiological processes by which certain animals can adapt their skin colors and features to resemble their immediate natural habitat; to conceive of means for using animal processes for camouflage uses; and to conduct experiments to establish whether adaptation is feasible, or even possible.
- Miscellaneous Systems - applied research and testing to: 1). establish whether magnetic fields and ultrasonic sound waves can induce a color shift and to correlate color play with stimuli parameters; 2.) assess the feasibility of such systems in terms of vehicular applications; 3.) demonstrate via appropriate models the practicality of reducing either or both of these concepts to practice, if possible.

- Concurrent Investigations - for each of the above recommended work programs, spectral measurements of the diffuse hemispherical reflectance of all materials and systems of materials should be accomplished in the spectral region from 0.2 to 20 μ ; spectral hemispherical measurements of the reflectance bands of liquid crystals should be made as a function of temperature and other stimulus parameters. A catalog of optical characterization data and performance information should be developed, which would also include estimates of costs, availability, and durability of materials, and other practical performance parameters.

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